Measurement of Vapor−Liquid Equilibria for the Pentafluoroethane + Propene Binary System from (263.15 to 323.15) K

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Isothermal vapor−liquid equilibrium (VLE) data were measured for the pentafluoroethane (CAS No. 354-33-6, R125) + propene (CAS No. 115-07-1, R1270) binary systems at five temperatures from (263.15 to 323.15) K using a circulation-type VLE apparatus. The uncertainties of the measured data were estimated to be ± 0.005 K for temperature, ± 600 Pa for pressure, and ± 0.001 in mole fraction for both the liquid and the vapor phases, respectively. The experimental data sets for the measured system were tested for thermodynamic consistency using procedures for high-pressure systems. The VLE data were correlated using the Peng−Robinson equation of state combined with the classical mixing rules. The calculated results agree well with the experimental data. The compositions of the azeotropes at each temperature for the binary system were also evaluated.

Introduction

Chlorofluorocarbons (CFCs) have been widely used as refrigerants, blowing agents, propellants, and cleaning agents due to their attractive properties. However, the production and usage of CFCs were prohibited by the international Montreal Protocol agreement and its amendments because of global environmental concerns.[1–3] Hydrofluorocarbons (HFCs) and related mixtures have been considered as promising alternatives because of their zero ozone-depletion potentials and low global-warming potentials. However, vapor−liquid equilibrium (VLE) data for these compounds are required as fundamental data for evaluating the performance of refrigeration cycles and determining the optimal compositions.[4,5]

Isothermal VLE data were measured for pentafluoroethane (R125) + propene (R1270) binary systems using a circulation-type VLE apparatus at (263.15, 278.15, 293.15, 308.15, and 323.15) K, with the uncertainties estimated to be ± 0.005 K for temperature, ± 600 Pa for pressure, and ± 0.001 in mole fraction for both the liquid and the vapor phases. R1270 is known for its per unit of swept volume refrigerating capacity, while the presence of R125, another promising alternative, restrains the flammability of R1270 and improved the thermodynamic properties. To our knowledge, VLE experimental data for the R125 (1) + R1270 (2) system are still not available in the literature.

The experimental VLE data showed good thermodynamic consistency. The data were then correlated using the Peng−Robinson equation of state (PR EoS)[6] with the classical mixing rules. The predictive ability of the model developed by Hou et al.[5] were further tested using the new experimentally studied system. The azeotropes at each temperature were also evaluated for the R125 (1) + R1270 (2) system.

Experimental Section

Chemicals. R125 was provided by the Zhejiang Institute of Chemical Research, while R1270 was provided by Beijing Zhaoge Gas Products Corporation. The purities of both chemicals were higher than 0.999 in mole fraction, as declared by the producers and verified by our GC analyses. The pure samples were degassed with liquid nitrogen before use to further improve their purities.

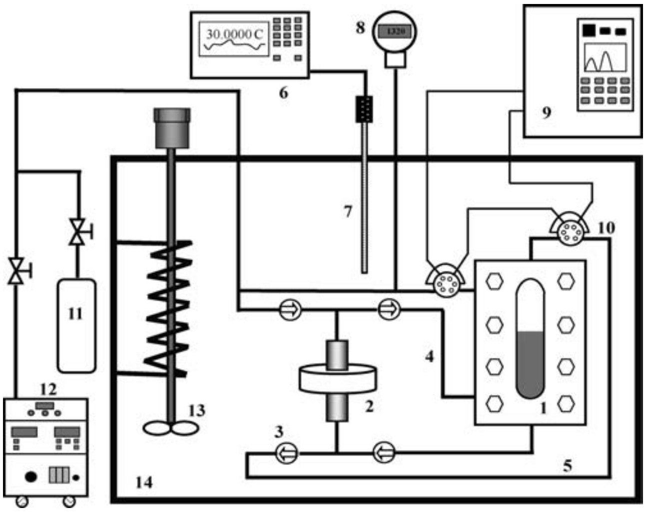

Figure 1. Schematic diagram of the VLE apparatus: 1, equilibrium cell; 2, magnetic pump; 3, check valve; 4, vapor sample circulating loop; 5, liquid sample circulating loop; 6, thermometry bridge; 7, platinum thermometer; 8, pressure transducer; 9, gas chromatograph; 10, high-pressure sampling valve; 11, sample cylinder; 12, vacuum pump; 13, stirrer; 14, thermostatic bath.

Apparatus. Isothermal VLE data were measured with a circulation-type apparatus. A schematic diagram of the apparatus is shown in Figure 1. The apparatus and experimental procedures were detailed and validated in our previous work.[7] The vapor and liquid samples were circulated with only one homemade magnetic pump. The circulation of the vapor and liquid samples was achieved by the upward and downward movements of the magnetic piston in the pump, which was driven by an external magnet moved by a speed-controllable motor. For the vapor circulation loop, when the magnetic piston of the pump is in a

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10.1021/je100049k

upward stroke, the pressure of vapor sample in the upward space of the pump increases. Thus, as shown in Figure 1, with the pressure difference, one check valve in the vapor circulation loop allows the sample in the pump to flow into the cell; then while the piston in a downward stroke, with the pressure difference, another check valve in the vapor circulation loop allows the sample in the cell to flow into the pump. A similar working pattern happens in the liquid circulation loop.

The temperature was measured with two sets of thermometry bridges (model: Hart 1590 and MI 6242T) and platinum resistance thermometers (model: Tinsley 5187SA), to ensure the reliability and accuracy of the temperature measurements. The total temperature measurement uncertainty was estimated to be within ± 0.005 K, including the uncertainty of the thermometry bridges (1 mK) and thermometers (2 mK) and the temperature fluctuation of the thermostat (3 mK). The pressure was measured with a Rosemount 3051S transducer, which was calibrated against two sets of absolute and relative digital monometers (model: Yokogawa MT210). The total pressure measurement uncertainty was estimated to be within ± 600 Pa.

During the experiment, samples of both the liquid phase and the vapor phase were taken out for analysis using high-pressure six-port valves (model: Rheodyne 7000 L) connected online to the equilibrium cell, using a 2 μL sample loop for the liquid sample and a 20 μL sample loop for the vapor sample. The samples were analyzed on a gas chromatograph (model: Shimadzu GC2014) using a thermal conductivity detector (TCD) and Porapak Q packed column (2.0 m long, 3.0 mm outer diameter, 80/100 mesh range). The oven and detector temperatures were set as (65 and 100) °C, respectively, to achieve the desirable separation effects. The gas chromatograph was calibrated using gravimetrically prepared sample mixtures, which were taken for GC analysis using another six-port valve (model: Valco C6W3). All three six-port valves were connected in series to allow the flow of helium gas (flow rate at 45 $\mathrm{mL \cdot min^{-1}}$). The overall uncertainty of the composition analysis was estimated to be ± 0.001 in mole fraction for both the liquid and the vapor phases, considering the reproducibility of GC and calibration results of GC.

Experimental Procedures. The apparatus was first evacuated to remove possible impurities. Then the system was flushed with R1270 and evacuated again to remove any traces of impurities. R1270 was first charged into the equilibrium cell, and then the entire system temperature was maintained constant by controlling the temperature of the thermostatic bath. The vapor pressure of R1270 was measured once the temperature stabilized. Then, a selected amount of R125 was charged into the equilibrium cell from another sample cylinder. The magnetic pumps were turned on to circulate both the vapor and the liquid samples in the equilibrium cell. The operation rate of the magnetic pump had little effect on the equilibrium composition as long as liquid drops and vapor bubbles could be seen inside the cell through the windows. The equilibrium state was first judged based on the pressure fluctuations and then further validated by the vapor and liquid sample composition variations. Generally, the equilibrium state was reached within an hour or so. Once equilibrium was reached, liquid and vapor samples were taken out for analysis through the sampling valves. Usually, four or five samples of each phase were taken for analysis to give average results. Then, the pressure in the equilibrium cell was measured after the magnetic pump was turned off. After this more R125 samples were charged into the apparatus to get another data point.

Table 1. Experimental and Calculated VLE Data for the R125 (1) + R1270 (2) System

T/K	x_1^{exp}	y_1^{exp}	p^{exp}/kPa	$y_1^{\mathrm{cal}a}$	$p^{\mathrm{cal}a}$/kPa
263.15	0	0	428.7	0	427.0
263.15	0.0817	0.1902	498.0	0.1865	494.0
263.15	0.2393	0.3557	556.0	0.3610	560.4
263.15	0.3873	0.4545	585.8	0.4552	586.1
263.15	0.5060	0.5216	589.3	0.5192	593.2
263.15	0.5270	0.5355	591.1	0.5306	593.5
263.15	0.6337	0.5990	591.0	0.5924	590.0
263.15	0.7297	0.6629	580.5	0.6586	578.8
263.15	0.7803	0.7102	567.5	0.7004	569.0
263.15	0.8126	0.7393	566.8	0.7304	561.1
263.15	0.9115	0.8418	531.1	0.8464	526.9
263.15	1	1	482.4	1	480.1
278.15	0	0	673.6	0	674.6
278.15	0.1779	0.2784	833.4	0.2917	837.9
278.15	0.2624	0.3556	877.2	0.3662	877.1
278.15	0.3684	0.4346	905.6	0.4403	907.6
278.15	0.4890	0.5104	921.5	0.5149	924.5
278.15	0.5577	0.5633	923.1	0.5574	927.0
278.15	0.6096	0.6009	925.0	0.5909	925.4
278.15	0.6934	0.6569	918.2	0.6500	916.1
278.15	0.7853	0.7258	902.5	0.7260	894.6
278.15	0.8424	0.7890	882.3	0.7821	874.1
278.15	1	1	782.1	1	780.4
293.15	0	0	1012.9	0	1016.2
293.15	0.0844	0.1522	1145.5	0.1614	1147.0
293.15	0.2112	0.2991	1263.6	0.3101	1271.2
293.15	0.3600	0.4186	1346.8	0.4291	1350.9
293.15	0.4648	0.4965	1376.4	0.5009	1379.8
293.15	0.5237	0.5398	1386.4	0.5407	1387.9
293.15	0.6142	0.6098	1390.8	0.6038	1389.2
293.15	0.6897	0.6711	1383.9	0.6607	1379.5
293.15	0.7266	0.6994	1376.0	0.6906	1370.8
293.15	0.7968	0.7663	1352.8	0.7528	1346.5
293.15	0.8954	0.8645	1299.7	0.8567	1292.5
293.15	1	1	1205.6	1	1204.8
308.15	0	0	1465.3	0	1471.3
308.15	0.0675	0.1249	1602.4	0.1224	1611.5
308.15	0.1268	0.2058	1703.8	0.2034	1707.9
308.15	0.2505	0.3361	1847.0	0.3306	1851.4
308.15	0.3517	0.4058	1929.0	0.4140	1927.4
308.15	0.5162	0.5385	1995.1	0.5371	1993.0
308.15	0.6450	0.6390	2005.8	0.6359	1999.6
308.15	0.7751	0.7513	1969.3	0.7472	1964.1
308.15	0.8408	0.8159	1930.6	0.8108	1928.2
308.15	0.9198	0.8994	1863.4	0.8971	1867.3
308.15	1	1	1773.2	1	1783.3
323.15	0	0	2047.9	0	2061.2
323.15	0.0595	0.1036	2205.5	0.1004	2225.6
323.15	0.1551	0.2262	2415.9	0.2213	2429.9
323.15	0.2631	0.3332	2589.5	0.3269	2595.3
323.15	0.4229	0.4631	2747.1	0.4597	2749.8
323.15	0.5445	0.5600	2813.7	0.5576	2807.6
323.15	0.6387	0.6381	2827.1	0.6362	2817.6
323.15	0.7169	0.7056	2813.6	0.7047	2801.9
323.15	0.7908	0.7754	2774.2	0.7733	2766.3
323.15	0.8631	0.8460	2713.5	0.8450	2711.3
323.15	1	1	2531.1	1	2549.3

[a] Calculated pressures and vapor phase compositions using the PR EoS and the classical mixing rules with the optimized binary interaction parameter k_{12}.

Results and Discussion

The VLE experimental data for the R125 (1) + R1270 (2) system at (263.15, 278.15, 293.15, 308.15, and 323.15) K are listed in Table 1.

Thermodynamic Consistency Tests for the VLE Data. Several kinds of thermodynamic consistency tests methods have been developed[8] for VLE data sets based on the different forms of the Gibbs−Duhem equation. The van Ness−Byer−Gibbs points test, which can take both the whole data set and the

Table 2. Thermodynamic Consistency Tests Results for the R125 (1) + R1270 (2) System

T/K	AAD (p)[a]	AAD (y_1)[b]	BIAS (y_1)[c]
263.15	0.414	0.0040	−0.0022
278.15	0.240	0.0050	0.0018
293.15	0.231	0.0045	−0.0021
308.15	0.061	0.0052	−0.0001
323.15	0.076	0.0045	0.0010

[a] $\mathrm{AAD}(p) = 1/N\sum_{i=1}^{N}|(p_i^{\mathrm{cal}} - p_i^{\mathrm{exp}})/p_i^{\mathrm{exp}}|\cdot 100$

[b] $\mathrm{AAD}(y_1) = 1/N\sum_{i=1}^{N}|y_{1,i}^{\mathrm{cal}} - y_{1,i}^{\mathrm{exp}}|$

[c] $\mathrm{BIAS}(y_1) = 1/N\sum_{i=1}^{N}(y_{1,i}^{\mathrm{cal}} - y_{1,i}^{\mathrm{exp}})$

individual data points into consideration, is widely used. This work uses a procedure similar to Jackson and Wilsak[9] using the van Ness−Byer−Gibbs points test for the high-pressure VLE data sets. The test makes use of the PR EoS to account for the vapor phase nonideality and the nonrandom two-liquid (NRTL) solution model[10] to account for the liquid-phase nonideality using liquid activity coefficients and neglects the differential of the total pressure term in the isothermal differential Gibbs−Duhem equation. The experimental data for p, T, and x_i along with the thermodynamic models were used to calculate the vapor-phase composition y_i, which were compared with the experimental data to check the thermodynamic consistency of VLE data sets.

Table 2 and Figures 2 and 3 show the thermodynamic consistency test results of the R125 (1) + R1270 (2) system at all five temperatures. The calculated deviations at the pressures in Table 2 and Figure 2 indicate that the pressure deviations are scattered consistently about zero, which means that the models used in the thermodynamic consistency test accurately describe the binary system. As shown in Table 2 and Figure 3, the deviations for the calculated and experimental vapor-phase compositions are mostly within the range of ± 0.01; thus, both of the error distributions and the average deviations indicate good thermodynamic consistency for all five data sets.

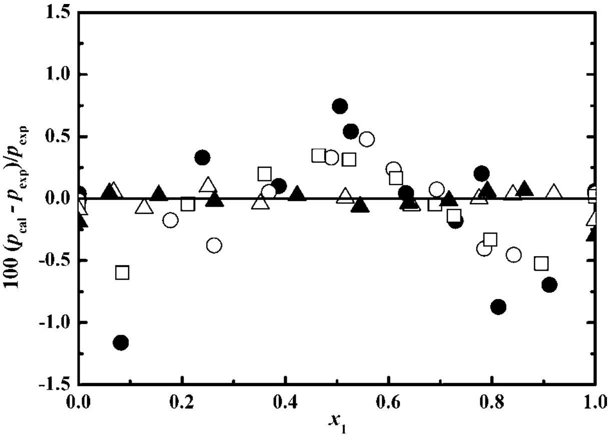

Figure 2. Thermodynamic consistency test results for the R125 (1) + R1270 (2) system: calculated pressure deviations: ●, 263.15 K; ○, 278.15 K; □, 293.15 K; △, 308.15 K; ▲, 323.15 K.

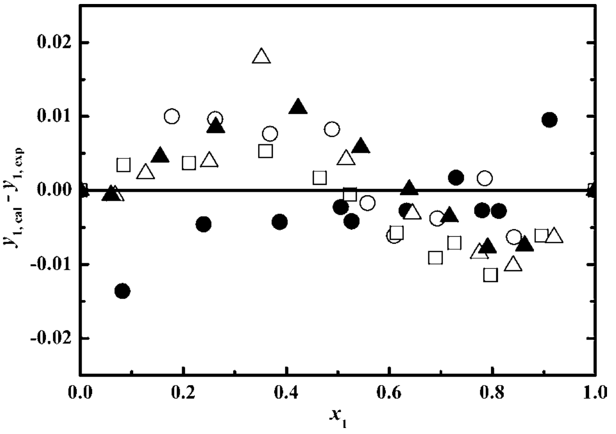

Figure 3. Thermodynamic consistency test results for the R125 (1) + R1270 (2) system: calculated vapor phase composition deviations: ●, 263.15 K; ○, 278.15 K; □, 293.15 K; △, 308.15 K; ▲, 323.15 K.

Table 3. Thermodynamic Properties for the Pure Compounds

compound	ASHRAE code	T_c/K	p_c/MPa	ω	ref
pentafluoroethane	R125	339.17	3.6177	0.3052	11
propene	R1270	364.21	4.555	0.1460	12

Table 4. Binary Interaction Parameters and Calculated Deviations for Pressure p and Vapor-Phase Composition y_1 for the R125 (1) + R1270 (2) System

T/K	k_{12}	100 $\Delta p/p$[a]	Δy_1[a]	100 $\Delta p/p$[b]	Δy_1[b]
263.15	0.104	0.51	0.0043	1.65	0.0103
278.15	0.101	0.36	0.0058	1.05	0.0085
293.15	0.100	0.30	0.0069	1.08	0.0096
308.15	0.097	0.28	0.0031	1.28	0.0060
323.15	0.099	0.41	0.0024	1.17	0.0051
overall	0.101	0.48	0.0045	1.25	0.0080

[a] Calculated average absolute deviations for the pressure and vapor-phase composition using the PR EoS and the classical mixing rules with the optimized binary interaction parameter k_{12}. [b] Calculated average absolute deviations for the pressure and vapor-phase composition using the predictive model of Hou et al.[5]

VLE Correlation Results. The PR EoS[6] with the classical mixing rules was chosen to correlate the VLE data for the R125 (1) + R1270 (2) binary system. Table 3 lists the critical properties and acentric factors for the pure compounds used in the VLE calculations.

The classical mixing rules with one adjustable parameter are:

$$a_{\mathrm{m}} = \sum_i \sum_j x_i x_j (1 - k_{ij})\sqrt{a_{ii}a_{jj}} \qquad (1)$$

$$b_{\mathrm{m}} = \sum_i \sum_j x_i x_j \frac{b_i + b_j}{2} \qquad (2)$$

where a and b are the energy parameter and covolume parameter in the PR EoS, respectively, x is the mole fraction for each component, and k_{ij} is the binary interaction parameter, which was obtained by performing isothermal bubble point calculations with the Levenberg−Marquardt optimization algorithm. The objective function (OF) used in the model parameter generalization was:

$$\mathrm{OF} = \sum_{i=1}^{N}\left(\frac{p_i^{\mathrm{exp}} - p_i^{\mathrm{cal}}}{p_i^{\mathrm{exp}}}\right)^2 \qquad (3)$$

where p_i^{exp} and p_i^{cal} are the experimental and calculated pressures, respectively, and N is the number of data points.

The calculated pressures and vapor-phase compositions are listed in Table 1 with the experimental values, while the optimized interaction parameters and the average calculated deviations at each temperature are listed in Table 4. As shown in Table 4 and Figure 4, the results show that the calculated values agree well with the experimental data. Figures 5 and 6 further illustrated the calculated pressure and vapor-phase composition deviations. The very small variation of the binary interaction parameter with temperature suggests that it can be assumed to be constant over a wide temperature range. Actually,

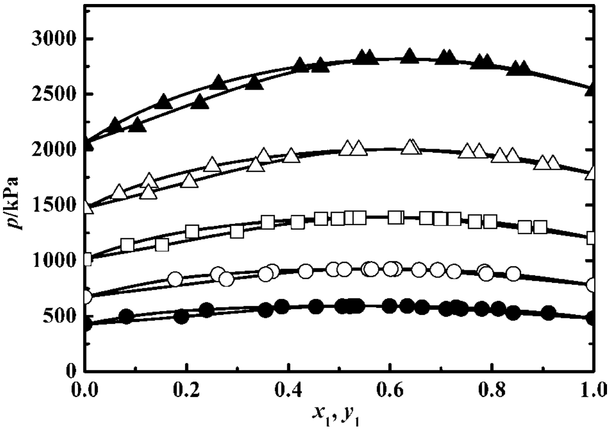

Figure 4. Pressure−composition diagram for the R125 (1) + R1270 (2) system: ●, 263.15 K; ○, 278.15 K; □, 293.15 K; △, 308.15 K; ▲, 323.15 K; −, calculated results.

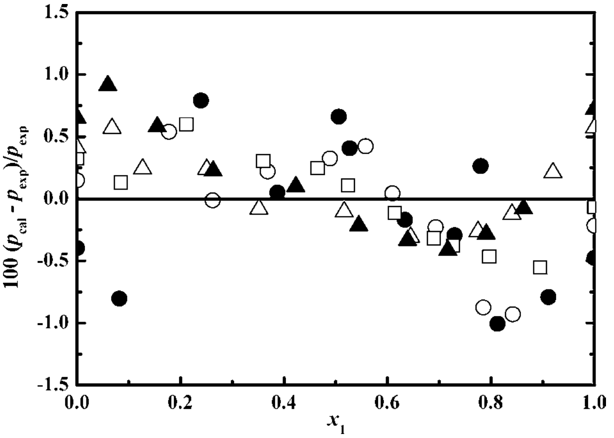

Figure 5. Calculated deviations for the pressure using the PR EoS and the classical mixing rules with the optimized binary interaction parameter k_{12}: ●, 263.15 K; ○, 278.15 K; □, 293.15 K; △, 308.15 K; ▲, 323.15 K.

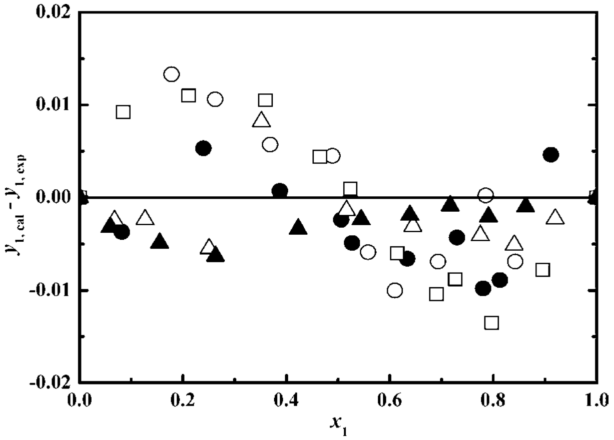

Figure 6. Calculated deviations for the vapor-phase composition using the PR EoS and the classical mixing rules with the optimized binary interaction parameter k_{12}: ●, 263.15 K; ○, 278.15 K; □, 293.15 K; △, 308.15 K; ▲, 323.15 K.

as shown in Table 4, when the data sets for all five isotherms were correlated together with one binary interaction parameter 0.101, the average pressure deviation and average vapor-phase composition deviation between experimental and calculated ones are 0.48 % and 0.0045, respectively.

Table 5. Azeotropic Pressures p^{azeo} and Compositions x_1^{azeo} for the R125 (1) + R1270 (2) System

T/K	x_1^{azeo}	p^{azeo}/kPa
263.15	0.5350	593.5
278.15	0.5568	927.0
293.15	0.5782	1390.3
308.15	0.6025	2001.9
323.15	0.6221	2818.1

The VLE data for the R125 (1) + R1270 (2) system was further represented using the predictive model developed by Hou et al.[5] for new refrigerant mixtures. With this group contribution model, both R125 and R1270 can be described by the developed group assignment strategy. The VLE prediction for the R125 (1) + R1270 (2) binary system is also possible because the group interaction parameters needed were already available.[5] The predictive results listed in Table 4 indicate that the predictive model is quite accurate and reliable with an average pressure deviation of 1.25 % and vapor-phase composition deviation of 0.0080, which further validates the developed group assignment strategy and optimized group interaction parameters.

Azeotropes for the R125 (1) + R1270 (2) System. As shown in Figure 4, the R125 (1) + R1270 (2) system forms azeotropes at all five temperatures studied in this work. The calculated azeotropic pressures and compositions are listed in Table 5. Both the azeotropic pressure and the composition change with temperature, with the pressure varying from (0.59 to 2.82) MPa and the compositions varying from 0.53 to 0.63 in the studied temperature range.

Conclusions

Vapor−liquid equilibria for the R125 (1) + R1270 (2) system were measured using a circulation-type apparatus at five temperatures. All of the data sets exhibited good thermodynamic consistency using the points test procedure. The VLE data can be well-correlated using the PR EoS with the classical mixing rules, while the predictive model of Hou et al. also gives very accurate VLE representations. The R125 (1) + R1270 (2) system exhibits positive homogeneous azeotropes at all five temperatures, and the azeotropic pressures and compositions of the binary system were calculated.

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Received for review January 17, 2010. Accepted April 19, 2010. This work was supported by the National Natural Science Foundation of China (50636020).

JE100049K